APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2005; **19**: 59–67
Materials, Nanoscience and Catalysis **AOC**
Published online in Wiley InterScience (www.interscience.wiley.com). DOI:10.1002/aoc.833

Cadmium *O*-alkylxanthates as CVD precursors of CdS: a chemical characterization

Davide Barreca[1]*, Alberto Gasparotto[2], Cinzia Maragno[2], Roberta Seraglia[1], Eugenio Tondello[2], Alfonso Venzo[1], Venkata Krishnan[3] and Helmut Bertagnolli[3]

[1]ISTM-CNR and INSTM, Department of Chemical Sciences, Padova University, Via Marzolo, 1-35131 Padova, Italy
[2]Department of Chemical Sciences, Padova University and INSTM, Via Marzolo, 1-35131 Padova, Italy
[3]Institut für Physikalische Chemie, Universität Stuttgart, Pfaffenwalding 55, D-70569 Stuttgart, Germany

Received 7 April 2004; Accepted 8 August 2004

Cadmium bis(*O*-alkylxanthates) are potential single-source molecular precursors for the chemical vapor deposition (CVD) of Cd(II) sulfide thin films. In this work, a multi-technique characterization of Cd(*O*-RXan)$_2$ compounds [where *O*-RXan is $CH_3CH_2OCS_2$ (*O*-EtXan) or $(CH_3)_2CHOCS_2$ (*O*-^{i}PrXan)] is performed by means of several analytical methods (extended x-ray absorption fine structure, Raman, Fourier transform infrared and optical absorption, spectroscopics ^{1}H and ^{13}C NMR, thermal analysis and mass spectrometry) for a thorough investigation of their structure and chemical–physical properties. The most important results concerning the chemical behavior under different experimental conditions, with particular attention to relevant properties for CVD applications, are presented and discussed. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: cadmium(II) bis(*O*-alkylxanthates); CdS; characterization; EXAFS; NMR; mass spectrometry

INTRODUCTION

Cadmium sulfide (CdS), a direct band-gap material ($E_g = 2.4$ eV),[1,2] has been employed extensively in thin-film transistors, X-ray detectors and photodiodes[3] and n-type window layers for solar cells.[4–6] For such applications, the system properties have been tailored by controlled modifications of the crystal structure[7,8] and morphology,[9] exploiting the versatility of suitable *bottom-up* synthetic routes. In this context, chemical vapor deposition (CVD) has attracted much attention as a possible method for the production of thin-film optoelectronic devices under mild and controlled conditions. A major role in tailoring material properties resides in a proper choice of the molecular precursors, whose nature strongly affects the composition, the microstructure and the morphology of the final product. In particular, single-source precursors containing all the elements to be deposited in a unique molecule[10,11] can be used conveniently as building-blocks for the single-step transformation of molecules into materials. The use of similar compounds offers significant advantages with respect to multiple-source reagents, such as a better film purity and an easier control of stoichiometry. Moreover, the material structure may be preformed already in the precursors by a suitable design of their molecular architecture. Examples of single-source precursors employed for the CVD of cadmium sulfide films include tris(alkyl)chalcogenophenolato complexes such as $Cd(SC_6H_2{}^tBu_3)_2$[12] and dialkyldithiocarbamates [$Cd(S_2CNRR')_2$], where R and R′ are alkyl groups.[11,13–15]

The present work is part of an extensive research activity in the CVD of metal sulfide thin films (ZnS, CdS, $Zn_xCd_{1-x}S$) from single-source *O*-alkylxanthate precursors.[16–18] Such compounds have been used previously in various fields, such as agents in metallurgy, accelerators in rubber vulcanization and high-pressure lubricants.[19,20] Nevertheless, to the best of our knowledge, cadmium(II) xanthates have not been employed as CVD precursors to date.

In this paper we describe the most relevant results concerning the synthesis and characterization of bis(*O*-ethyl) and bis(*O*-isopropyl) cadmium xanthates Cd(*O*-EtXan)$_2$ and Cd(*O*-^{i}PrXan)$_2$, where *O*-EtXan is $CH_3CH_2OCS_2$ and *O*-^{i}PrXan is $(CH_3)_2CHOCS_2$. In addition to their appreciable volatility and stability to air and moisture, the presence of pre-formed Cd–S bonds and the absence of Cd–C bonds enable their clean conversion into cadmium(II) sulfide in an

---

*Correspondence to: Davide Barreca, ISTM-CNR and INSTM, Department of Chemical Sciences, Padova University, Via Marzolo, 1-35131 Padova, Italy.
E-mail: barreca@chin.unipd.it

Copyright © 2004 John Wiley & Sons, Ltd.

inert atmosphere. Moreover, they allow toxic multiple-source systems to be avoided and better control over the composition and microstructure of the final product to be achieved.[16] Previous investigations have focused mainly on the structural features of both Cd(*O*-EtXan)$_2$ and Cd(*O*-^{i}PrXan)$_2$,[19,21–23] but further studies are necessary to elucidate structure–property relationships, with particular regard to the chemistry of CVD processes.

The main focus of the present work is a thorough chemical characterization of Cd(*O*-RXan)$_2$ compounds (R = Et, ^{i}Pr), aimed at obtaining valuable information on their chemical–physical characteristics. A similar objective can be pursued only by the use of complementary analysis techniques, allowing investigation of the chemical behavior of the above complexes in the gas phase, in solution and in the solid state. In particular, the coordination geometry was investigated by extended X-ray absorption fine structure (EXAFS) and their chemical structure in solid state was analyzed by the combined use of Fourier transform infrared (FTIR) and Raman spectroscopics. Chemical information on Cd(*O*-RXan)$_2$ was obtained by NMR spectroscopic methods, whereas optical properties were studied by UV–Vis absorption. Because the ultimate goal of the present research activity is the use of Cd(*O*-RXan)$_2$ compounds as CVD precursors for CdS films, attention was focused on the study of their thermal decomposition and gas-phase behavior by means of thermal analyses such as thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), and by different mass spectrometric techniques, such as electrospray ionization (ESI),[24] electron ionization (EI) and mass-analyzed ion kinetic energy (MIKE) experiments.[25]

RESULTS AND DISCUSSION

Cadmium bis(*O*-alkylxanthate) complexes were synthesized according to a literature procedure[22,26] and checked for purity by elemental analysis. In the monoclinic X-ray crystal structure of both Cd(*O*-EtXan)$_2$ and Cd(*O*-^{i}PrXan)$_2$, the coordination around each Cd(II) center is a distorted tetrahedron, with the Cd atoms nearly equidistant from the four S atoms.[22,23] Each S atom is associated with a different xanthic group, i.e. all the ligands bridge two cadmium atoms to form a two-dimensional network. The resulting layers are stacked along the *a*-axis.[21]

In order to attain a deeper insight into the coordination geometry related to xanthate compounds, EXAFS spectroscopy has been proved to be a very useful analytical tool. Until recently, only very few literature reports are available on these investigations.[27,28] In the case of Cd(*O*-^{i}PrXan)$_2$, the experimentally determined and theoretically fitted EXAFS functions in *k* space and their Fourier transforms in real space for the above compound are shown in Fig. 1. The corresponding structural parameters are summarized in Table 1.

In the analysis of the experimental k^3-weighted $\chi(k)$ function, only the first shell consisting of about four sulfur backscatterers could be fitted at a distance of about 2.54 Å. The other shells could not be determined because their

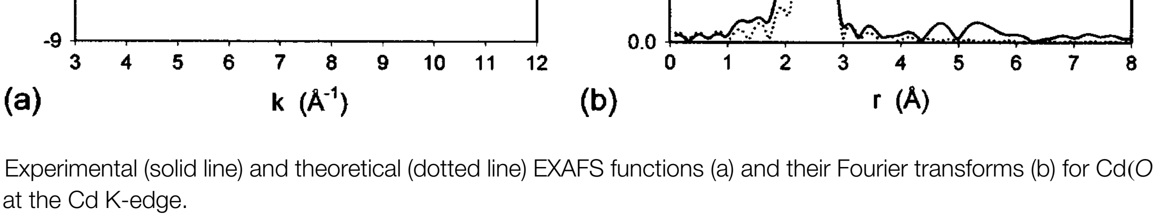

Figure 1. Experimental (solid line) and theoretical (dotted line) EXAFS functions (a) and their Fourier transforms (b) for Cd(*O*-^{i}PrXan)$_2$ measured at the Cd K-edge.

Table 1. Structural parameters of Cd(*O*-^{i}PrXan)$_2$ obtained by EXAFS analysis

Absorber–backscatterer distance	Coordination number N	Interatomic distance (Å)	Debye-Waller factor σ (Å)	Threshold energy shift ΔE_0 (eV)	k range (Å^{-1})	Fit index
Cd–S	4.3 ± 0.4	2.54 ± 0.03	0.063 ± 0.006	15.79	3.0–12.0	24.95

Copyright © 2004 John Wiley & Sons, Ltd.

contribution to the EXAFS function was insignificant. The Debye-Waller factor, which accounts for the static and vibrational disorders in the system, was found to be 0.063 Å. The obtained Cd–S distance and the coordination number were in good agreement with those of crystalline cadmium sulfide,[29] suggesting that Cd(*O*-^{i}PrXan)$_2$ is potentially very promising as a single-source CVD precursor for CdS thin films.

The Raman spectrum of Cd(*O*-^{i}PrXan)$_2$ (Fig. 2) showed a variety of interesting signals and the results were in good agreement with those obtained by FT-IR measurements (Fig. 3). Both Raman and FTIR assignments, based on the literature data,[30–35] are summarized in Table 2. In the FTIR spectrum (Fig. 3), the most intense bands were observed at ~1030, 1094 and 1208 cm^{-1} and attributed to CS_2, CCC and COC out-of-phase stretching vibrations, respectively. The CS_2 in-phase stretching was well evident in the Raman spectrum around 650 cm^{-1} (Fig. 2). Other prominent signals in Fig. 2 were attributed as follows: 75 and 87 cm^{-1}, lattice vibrations; 473 cm^{-1}, COC and CCC in-phase bending vibrations; 1030 cm^{-1}, CS_2 out-of-phase stretching vibrations. The vibrational disorder, calculated basing on the Cd–S vibration at 246 cm^{-1}, using standard statistical mechanics

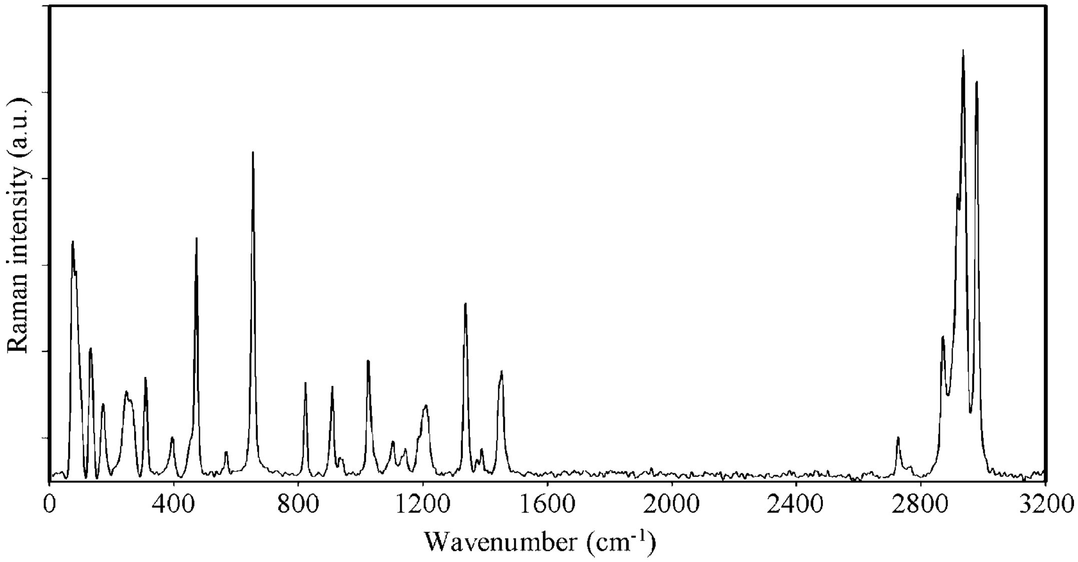

Figure 2. Raman spectrum of Cd(*O*-^{i}PrXan)$_2$.

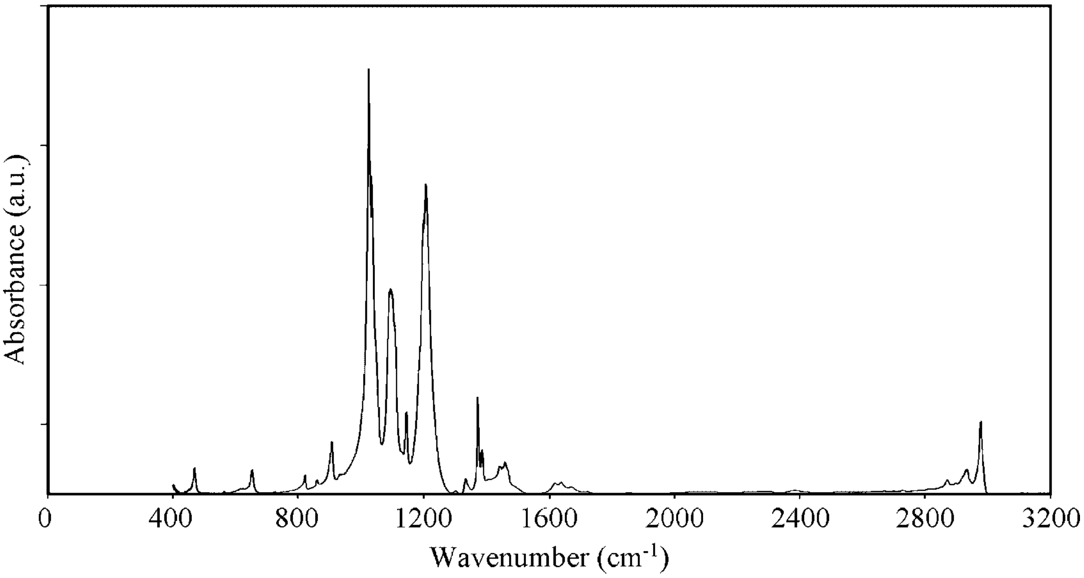

Figure 3. FTIR spectrum of Cd(*O*-^{i}PrXan)$_2$.

Table 2. Selected features and corresponding assignments in the vibrational spectra of Cd(*O*-^{i}PrXan)$_2$

Raman frequency (cm^{-1})	Infrared frequency (cm^{-1})	Assignment
75, 87		Lattice vibrations
132		Cd–S vibrations
173		CS_2 rocking Cd–S vibrations
246, 262		Cd–S stretching vibrations
309		SCS, CCC in-phase bending
397		CCC, SCS out-of-phase bending Cd–S vibrations
473	468	COC, CCC in-phase bending
569	572	OCS_2 wagging
655	652	CS_2 in-phase stretching
825	821	OCC_2 in-phase stretching
909	907	CH_3 out-of-phase rocking perpendicular to OC(H)
1030	1025, 1034	CS_2 out-of-phase stretching
1110	1094	CCC out-of-phase stretching
1150	1144	CH_3 rocking, (S)CO stretching
1208	1208	COC out-of-phase stretching
1338	1333	CH wagging
1390	1372, 1385	CH_3 in-phase deformation
1455	1460	CH_3 out-of-phase deformation
2878	2871	CH_3 in-phase stretching
2940	2932	CH_3 out-of-phase stretching
2980	2977	CH_3 out-of-phase stretching

equations,[36] was 0.064 Å, in close agreement with the Debye-Waller factor found from EXAFS measurements. This result suggests that the major component of disorder in the system is due to vibrations rather than to static displacements.

The Cd bis(*O*-alkylxanthate) compounds were subjected also to a characterization in solution by means of optical absorption spectroscopy and NMR techniques. For both Cd(*O*-EtXan)$_2$ and Cd(*O*-^{i}PrXan)$_2$, the optical absorption spectra in methanol solutions (Fig. 4) were characterized by two intense bands at ~230 and ~300 nm, assigned respectively to $n \rightarrow \sigma^*$ and $n \rightarrow \pi^*$ transitions of the xanthate group.[37] The shoulder present at ~315 nm in both spectra was assigned to $\pi \rightarrow \pi^*$ absorptions. No absorption was observed at wavelengths >350 nm. This attribution was further confirmed by the presence of similar absorptions in other metal xanthates, allowing any contribution from the metal center to be ruled out.[38] Moreover, the present results indicated little influence of the R group (R = Et, ^{i}Pr) on the optical absorption properties.

The NMR spectra of 0.1 M Cd(*O*-EtXan)$_2$ or Cd(*O*-^{i}PrXan)$_2$ in DMSO-d_6 ($\varepsilon = 32$) indicated that in solution all the xanthate units are equivalent. In the case of the isopropyl derivative, the signals of the methyl (C*H*$_3$) and methyne (C*H*) protons were observed at δ 1.276 and 5.106 (doublet and septet), respectively. The corresponding ^{13}C resonances appeared at δ 21.75 and 80.96, in addition to a signal for the dithiocarbonyl carbon at δ 228.48. For Cd(*O*-EtXan)$_2$, the proton signals were located at δ 1.285 (C*H*$_3$) and δ 4.319 (C*H*$_2$), and the ^{13}C signals at δ 14.61 (CH_3), 72.76 (CH_2) and 229.62 (CS_2).

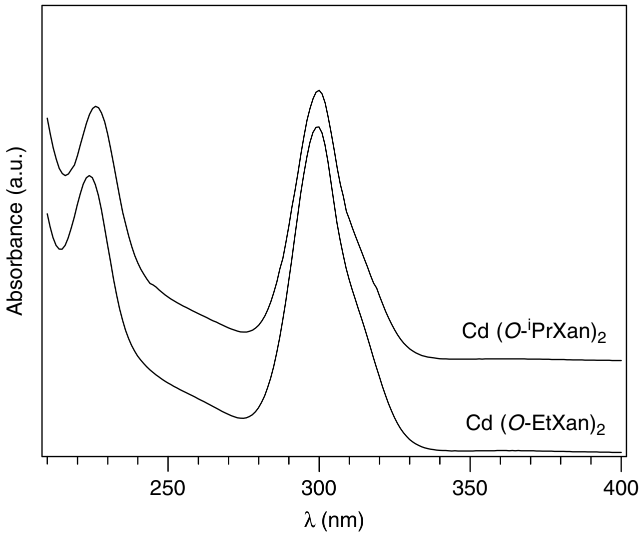

Figure 4. Optical absorption spectra of Cd(*O*-EtXan)$_2$ and Cd(*O*-^{i}PrXan)$_2$. Measurements were carried out on 5×10^{-5} M ethanolic solutions.

When the less polar $CDCl_3$ ($\varepsilon = 4.8$) was used as solvent, the solubility of the xanthates was much lower. Nevertheless, for Cd(*O*-^{i}PrXan)$_2$ one doublet at δ 1.463 (C*H*$_3$ protons) and a septet at δ 5.293 (C*H* proton) were detected. The corresponding ^{13}C resonances appeared at δ 21.51 and 84.24, respectively, together with the signal due to the thiocarbonyl ^{13}C nucleus at δ 229.04. For Cd(*O*-EtXan)$_2$, the resonances of the methyl protons appeared at δ 1.484, and those of the corresponding methylene protons at δ 4.540. The ^{13}C resonances were observed at δ 13.88 (CH_3 carbons), 75.26 (CH carbons) and 231.01 (CS_2 carbons), respectively. Taken together, these observations confirmed the purity of the synthesized compounds and indicated a low solvent influence on the NMR response.

The reactivity of Cd(*O*-EtXan)$_2$ and Cd(*O*-^{i}PrXan)$_2$ was then investigated, with particular attention to the chemistry of CVD processes. In this context, the attention was focused on their thermal behavior in an inert atmosphere and on mass spectrometric analyses. The thermogravimetric curves for Cd(*O*-EtXan)$_2$ (Fig. 5a) and Cd(*O*-^{i}PrXan)$_2$ (Fig. 5b) recorded under nitrogen flow displayed a qualitatively similar trend. In fact, at temperatures higher than 120 °C both compounds underwent a significant mass loss (T = 164 °C and 169 °C for Cd(*O*-EtXan)$_2$ and Cd(*O*-^{i}PrXan)$_2$, respectively), corresponding to an endothermic process

Copyright © 2004 John Wiley & Sons, Ltd.

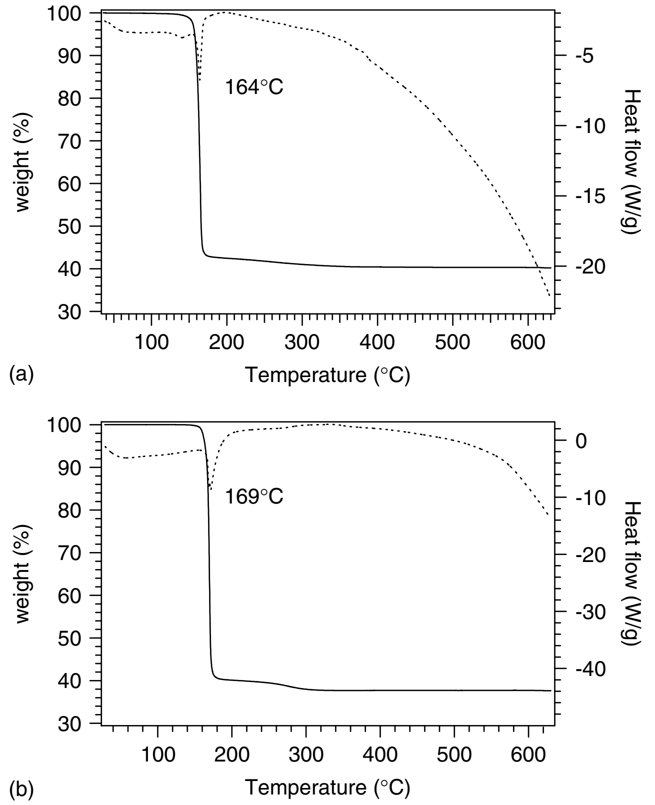

Figure 5. TGA (solid line) and DSC (dotted line) traces of Cd(*O*-EtXan)$_2$ (a) and Cd(*O*-^{i}PrXan)$_2$ (b).

ascribed to the sample vaporization. In the next region (200–300 °C), a second weight loss occurred, leading to a constant mass for $T \geq 300$ °C. The final weight values of 40.9% for Cd(*O*-EtXan)$_2$ and 37.4% for Cd(*O*-^{i}PrXan)$_2$ agreed to a good extent with those theoretically expected for the formation of CdS, indicating that the bis(*O*-alkylxanthate) Cd derivatives might be regarded as interesting single-source precursors for the CVD of cadmium sulfide films under an inert atmosphere. Recently, some of us reported very similar results for the transformation of Zn(*O*-EtXan)$_2$ into zinc(II) sulfide.[16]

To characterize further the structure of cadmium bis(*O*-alkylxanthates), mass spectrometric analyses were undertaken using ESI,[24] a 'soft' ionization technique, and EI, a 'hard' ionization technique. Because cadmium bis(*O*-alkylxanthates) have a polymeric structure in the solid state (see above), oligomeric gas-phase species might be destroyed by EI ionization conditions. Therefore, a 'softer' ionization technique such as ESI[24] is a useful analytical tool to assess the presence of oligomers. The coupling of EI-MS and ESI-MS characterizations yielded valuable information on the compound fragmentation patterns and on the relative stability of Cd–S bonds.

The ESI mass spectra of Cd(*O*-RXan)$_2$ were recorded in both positive and negative modes 10^{-6} M sample solutions in chloroform were injected directly into the ESI ion source via a syringe pump at a flow rate of 8 μl min^{-1}. The negative ion ESI mass spectra are reported in Fig. 6. For both complexes the Cd(*O*-RXan)$_3^-$ ions have been detected as clusters, due to the eight Cd isotopes, centered at m/z 519 for R = ^{i}Pr (Fig. 6a) and at m/z 477 for R = Et (Fig. 6b). In contrast of what is expected using this 'soft' ionization technique, several peaks were detected even on changing analysis conditions such as solvent, concentration and source potential. The presence of some ionic species can be explained by subsequent CS$_2$ losses directly from the *pseudo*molecular ions (labeled with an asterisk in Fig. 6). Furthermore, other signals (labeled • in Fig. 6) were detected and ascribed to R loss (R = Et, ^{i}Pr) with H rearrangements from the *pseudo*molecular ion, followed by subsequent CS$_2$ loss. The MS^n experiments carried out on the *pseudo*molecular ions showed that their most favored decomposition pathways were due to successive CS$_2$ losses.

The positive ion ESI mass spectra were simpler than those obtained in negative ion mode. As shown in Fig. 7, the spectra were characterized by an intense peak centered at m/z 631 for Cd(*O*-^{i}PrXan)$_2$ (Fig. 7a) and at m/z 589 for Cd(*O*-EtXan)$_2$ (Fig. 7b). These ions corresponded to dinuclear ionic species of general formula Cd$_2$(*O*-RXan)$_3^+$, as confirmed by the good agreement between theoretical and experimental isotopic clusters.

The results obtained by ESI-MS analysis suggested that, under ESI conditions, the Cd–S bond strength was lower than that for C–S. For this reason, the more favored decomposition processes of Cd(*O*-RXan)$_2$ complexes (R = Et, ^{i}Pr) involve subsequent CS$_2$ losses, as discussed previously (Fig. 6).

In order to investigate the fragmentation patterns of Cd bis(*O*-alkylxanthates) in the gas phase, i.e. under experimental conditions more similar to those commonly adopted in CVD processes, the Cd(*O*-RXan)$_2$ complexes were analyzed by EI. The EI mass spectra were characterized by the presence of M$^{+\cdot}$ clusters centered at m/z 380 and 356 for Cd(*O*-^{i}PrXan)$_2$ and Cd(*O*-EtXan)$_2$ respectively. As an example, the EI mass spectrum of Cd(*O*-EtXan)$_2$ is reported in Fig. 8a. A part from the molecular ions, a cluster centered at m/z 235 was observed and attributed to a ligand loss from M$^{+\cdot}$, whereas in the low mass range the peaks centered at m/z 122 and 114 corresponded to [HOEtXan]$^{+\cdot}$ and Cd$^{+\cdot}$, respectively. The ions at m/z 134 and 150 could be attributed to ionic species originating from rearrangements of the ligands, being completely absent from the typical Cd isotopic cluster. The MIKE experiments[25] carried out on the M$^{+\cdot}$ ions of Cd(*O*-EtXan)$_2$ (selecting the ions containing the ^{110}Cd isotope) led to the spectrum reported in Fig. 8b. The most favored decomposition pathway was due to the formation of Cd$^{+\cdot}$ at m/z 110, and the CdS$^{+\cdot}$ ions were detected at m/z 142. The ligand loss from M$^{+\cdot}$ led to the ionic species at m/z 231, and the ion at m/z 203 corresponded to CdS$_2$COH$^+$. Analogous fragmentation processes were observed for Cd(*O*-^{i}PrXan)$_2$.

It is worthwhile observing that, in contrast to the results obtained under ESI conditions, no ionic species arising from CS$_2$ losses were ever detected under EI conditions

Copyright © 2004 John Wiley & Sons, Ltd.

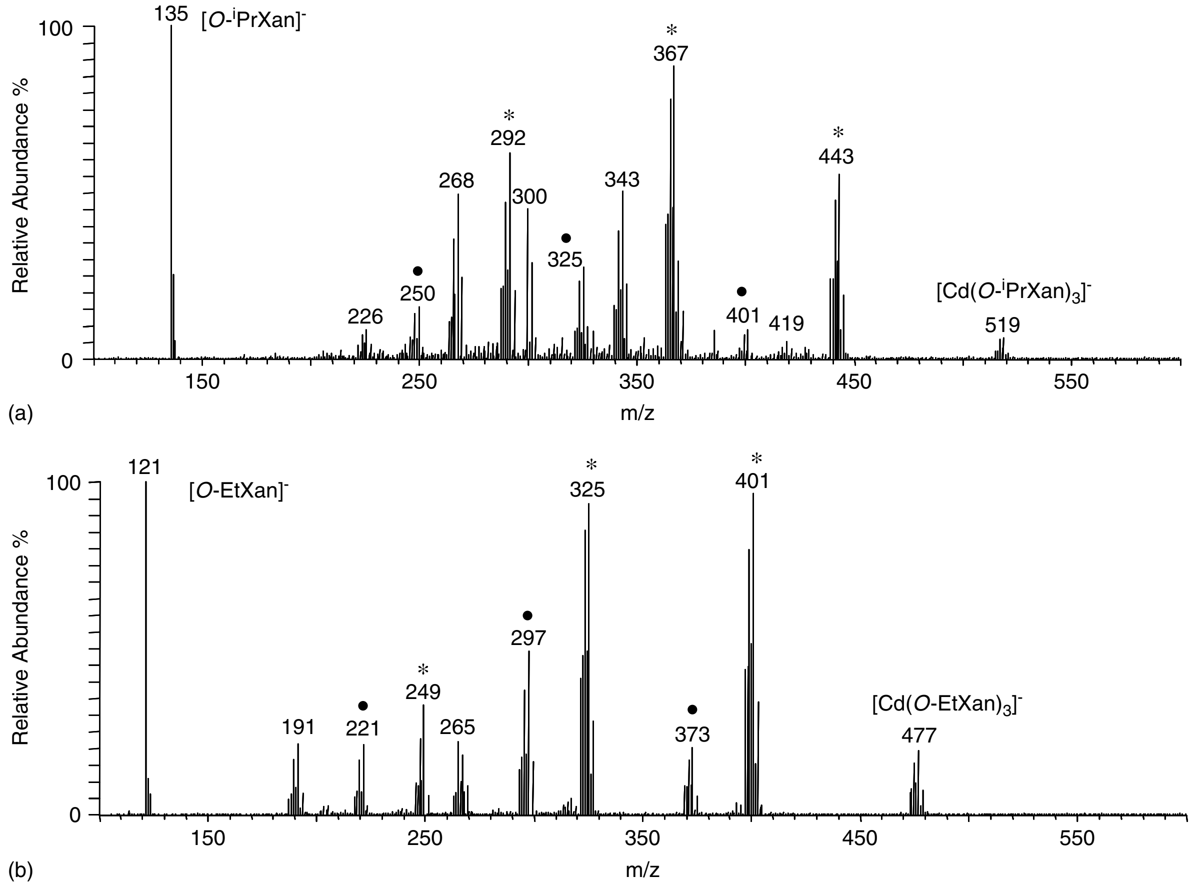

Figure 6. Negative ion ESI mass spectra of chloroform solutions of Cd(*O*-^{i}PrXan)$_2$ (a) and Cd(*O*-EtXan)$_2$ (b).

and MIKE experiments. This difference suggests that the ESI ionization technique can activate several decomposition pathways in bis(*O*-alkylxanthate) compounds, due to both ionization mechanisms and interaction with solvent that made the Cd–S bond weaker than in the solid or gas phase. This hypothesis was corroborated by the fact that preliminary CVD experiments[17] in a nitrogen atmosphere from Cd(*O*-^{i}PrXan)$_2$ yielded the formation of CdS films at substrate temperatures of 200–500 °C, showing that the core structure of the precursor (i.e. Cd coordinated to four sulfur atoms) effectively represents the building-block for the solid-state structure of CdS. On this basis, it might be concluded that Cd–S moieties were relatively stable in the gas phase, thus indicating their suitability as CVD single-source precursors for CdS.

CONCLUSIONS

This work was dedicated to a thorough characterization of cadmium bis(*O*-alkylxanthates), Cd(*O*-RXan)$_2$, where *O*-RXan is $CH_3CH_2OCS_2$ (*O*-EtXan) or $(CH_3)_2CHOCS_2$ (*O*-^{i}PrXan). In view of their potential application as single-source precursors for the CVD of CdS, their structure–property relationships were analyzed by means of a multi-technique approach, both in the solid state (FTIR, Raman, EXAFS) and in solution (optical absorption, ^{1}H and ^{13}C NMR). Moreover, thermal analyses (TGA, DSC) and mass spectrometry (ESI, EI) were used to investigate the thermal behavior and fragmentation pattern of the above compounds.

The FTIR and Raman spectroscopies allowed a fingerprint identification of Cd(*O*-EtXan)$_2$ and Cd(*O*-^{i}PrXan)$_2$, and EXAFS investigation revealed a Cd–S distance similar to that of crystalline CdS, which is a very interesting feature for the use of such compounds in CVD applications where the precursor core structure represents the building-block of the desired material. Moreover, thermal analyses indicated the possibility of obtaining CdS by thermal decomposition of Cd(*O*-RXan)$_2$ compounds in an inert atmosphere. For both complexes, ESI-MS analyses pointed out the subsequent losses of CS_2 from the *pseudo*molecular ion, whereas EI-MS investigation showed no similar processes. Such a feature might be ascribed to a sort of *solvent effect*, resulting in a weakening of the Cd–S bonds with respect to C–S bonds in solution. Very little influence of the R group (R = Et, ^{i}Pr) on the behavior of Cd(*O*-RXan)$_2$ compounds was observed. In summary, the results reported in the present work indicate the

Copyright © 2004 John Wiley & Sons, Ltd.

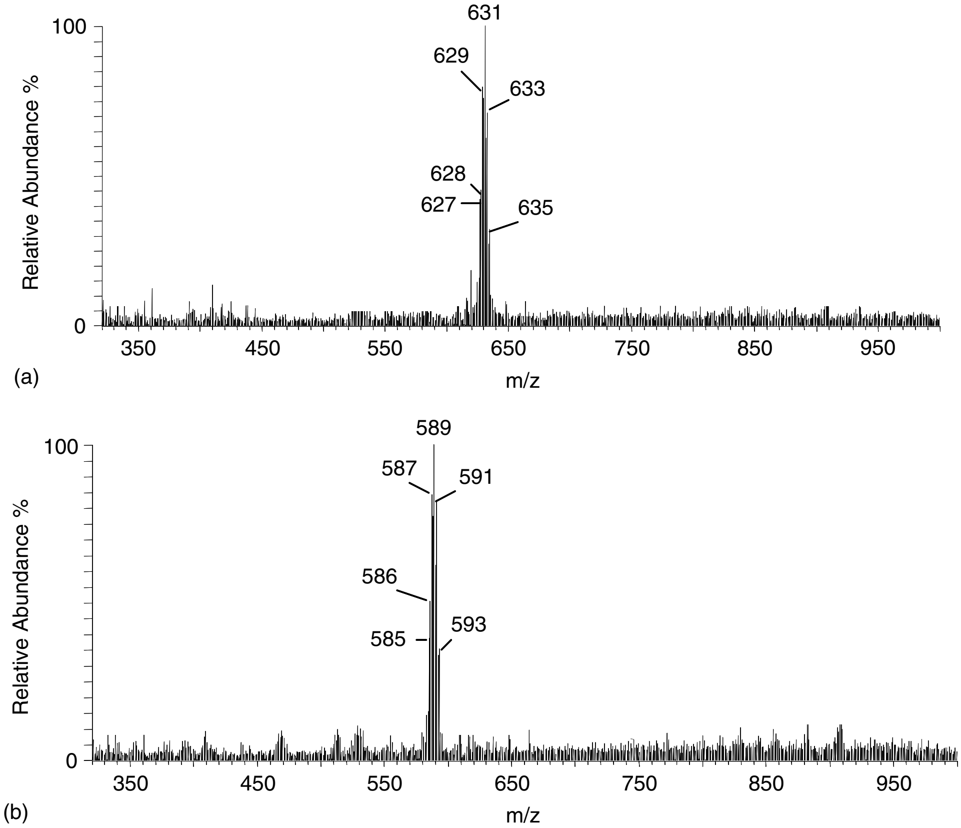

Figure 7. Positive ESI mass spectra of chloroform solutions of Cd(O-^{i}PrXan)$_2$ (a) and Cd(O-EtXan)$_2$ (b).

suitability of cadmium bis(*O*-alkylxanthates) as single-source CVD precursors for CdS thin films.

EXPERIMENTAL

Synthesis

The Cd(O-RXan)$_2$ compounds were synthesized following a previously established literature procedure.[22,26] Potassium hydroxide (KOH, Aldrich, 25.0 mmol) was ground to a fine powder and placed in a flask where a slight excess of ROH (R = Et or ^{i}Pr, Aldrich) was added. The mixture was stirred until the solid was completely dissolved (~2 h). After carbon disulfide addition (CS_2, Aldrich, 25 mmol, 1.5 cm^3), the mixture was stirred for 1 h to give a pale yellow solution. Deionized water (10 cm^3) was added, leading to the final formation of light-yellow needles of potassium *O*-alkylxanthate K(S_2COR), where R = Et or ^{i}Pr (yield ~85%).

An aqueous solution of K(S_2COR) (22 mmol in 30 cm^3 of H_2O) was added to a solution of cadmium(II) chloride ($CdCl_2$, Aldrich, 11 mmol in 50 cm^3 of H_2O). A white flocculent precipitate formed immediately. The mixture was stirred for 1 h, subsequently vacuum-filtered and finally dried to obtain a white powder (yield ~82%). Because the compounds obtained were slightly photosensitive, precautions were taken during preparation and storage to avoid light exposure.

Elemental analyses

Cd(O-EtXan)$_2$. Found: C, 20.3%; H, 2.3%; S, 37.0%. Calculated: C, 20.3%; H, 2.8%; S, 36.2%. Cd(O-^{i}PrXan)$_2$. Found: C, 25.1%; H, 3.6%; S, 32.9%. Calculated: C, 25.1%; H, 3.7%; S, 33.1%.

Characterization

The EXAFS measurements were performed at the Hamburger Synchrotronstrahlungslabor (HASYLAB) at DESY, Hamburg. Cadmium bis(*O*-isopropylxanthate) was measured with an Si(311) double-crystal monochromator at the Cd K-edge at 26711 eV under ambient conditions. Data were collected in transmission mode with ion chambers filled with argon, and energy calibration was monitored with a 20 μm thick Cd metal foil. The samples were prepared as pellets of a mixture of the compound and polyethylene. The concentration of the samples was adjusted to yield an extinction of 1.5.

Data were analyzed with a specially developed program package.[39] Program AUTOBK[40] was used for background removal and program EXCURV92[41] was used for evaluation of the EXAFS function. Data analysis in *k*-space was performed according to the curved-wave formalism with XALPHA phase and amplitude functions, and the resulting

Copyright © 2004 John Wiley & Sons, Ltd.

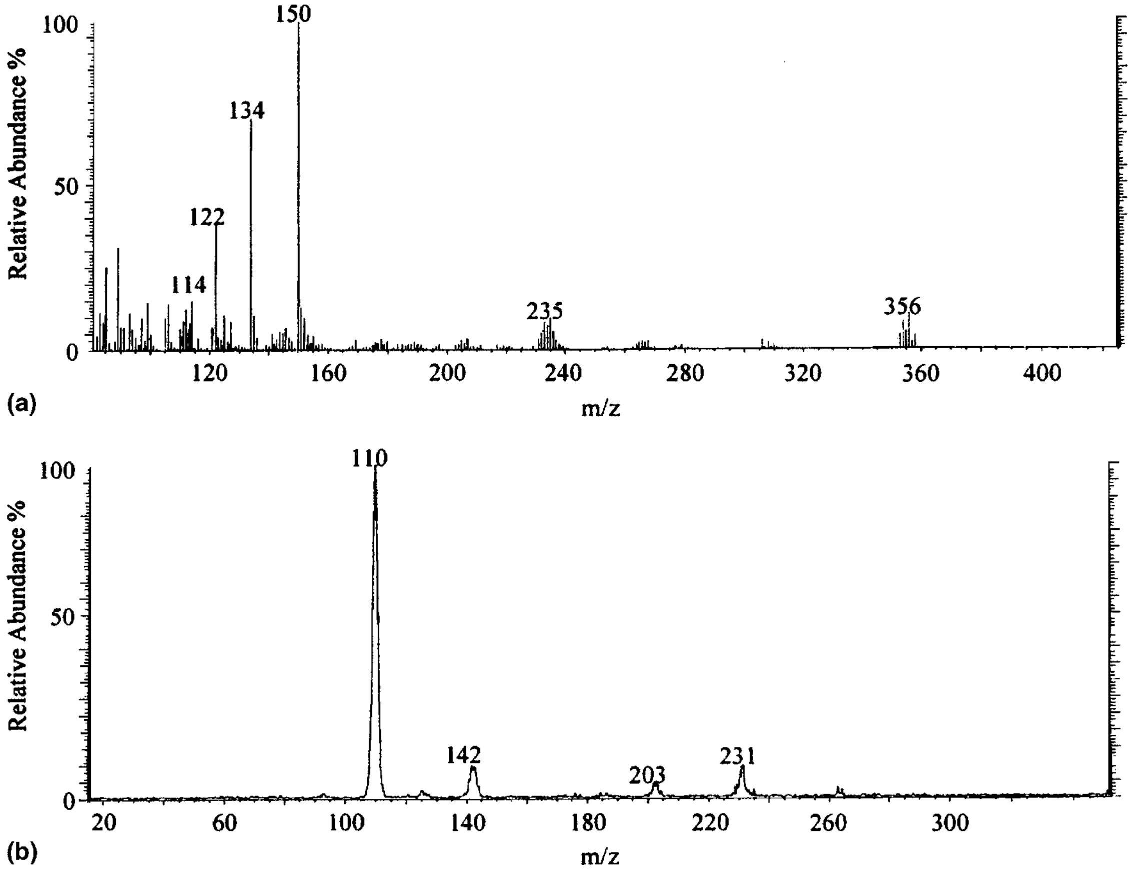

Figure 8. (a) EI mass spectrum of Cd(*O*-EtXan)$_2$. (b) MIKE spectrum of the corresponding $M^{+\cdot}$ ions at *m/z* 356.

EXAFS function was weighted with k^3. The mean free path of the scattered electrons was calculated from the imaginary part of the potential (V_{PI} set to -4.00) and an overall energy shift of ΔE_0 was introduced to fit the data. The amplitude factor was fixed at 0.4 for the analysis based on CdS, which was measured along with the sample as a reference material. The optimized parameters were coordination number, absorber–backscatterer distance, Debye-Waller factor and energy shift.

Raman spectra were recorded on a Bruker RFS 100/S Fourier transform Raman spectrometer (spectral resolution 4 cm^{-1}) with an air-cooled near-infrared Nd:YAG laser (wavelength = 1064 nm, power = 150 mW). The scattered light was collected with a high-sensitivity Ge diode (cooled with liquid nitrogen). For averaged measurements, 1024 scans were accumulated.

The FTIR spectra were obtained by means of a Bruker IFS 66v/S FTIR spectrometer with a DLATGS detector in absorption mode with a spectral resolution of 2 cm^{-1}. The samples were prepared as KBr pellets and measured under ambient conditions (512 scans).

Optical absorption spectra were recorded in the range 200–800 nm on a Cary 5E (Varian) UV–Vis–NIR dual-beam spectrophotometer with a spectral bandwidth of 1 nm. Measurements were carried out in quartz cuvettes (optical path 0.5 mm) containing 5×10^{-5} M ethanolic solutions.

The ^{1}H and ^{13}C NMR spectra were recorded on CDCl$_3$ and (CD$_3$)$_2$SO (DMSO) solutions at 298 K on a Bruker Avance 400 NMR spectrometer at $\nu_o = 400.13$ and 100.61 MHz, respectively. The chemical shift values are given in ppm against internal Me$_4$Si. Thermal analyses were made using an SDT 2960 apparatus from TA Instruments (New Castle, USA), which allows simultaneous DSC–TGA measurements to be performed. The analyses were recorded under N$_2$ flow (heating rate = 10 °C min^{-1}) to prevent undesired oxidation reactions on heating the sample powders.

The ESI mass spectra were obtained using an LCQ instrument (Finnigan, Palo Alto, CA, USA) operating in both positive and negative ion modes. The entrance capillary temperature was 200 °C and the capillary voltage was kept at ±5 kV. Solutions (at a concentration of $\sim 10^{-6}$ M) were introduced by direct infusion using a syringe pump at a flow rate of 8 µl min^{-1}. The He pressure inside the trap was kept constant. The pressure read directly by ion gauge (in the absence of the N$_2$ stream) was 2.8×10^{-5} Torr.

The EI measurements were performed on a VG AutoSpec mass spectrometer (Micromass, Manchester, UK) operating

Copyright © 2004 John Wiley & Sons, Ltd.

under EI conditions of 70 eV, 200 μA and an ion source temperature of 200 °C.

Metastable ionic species were detected by MIKE spectrometry.

Acknowledgments

Professor T.R. Spalding (University College, Cork, Ireland) is gratefully acknowledged for help in the synthesis of the precursor compounds. Special thanks are due to Dr R. Saini for experimental assistance in thermal analysis and to Ms J. Hollmann for her help in FTIR measurements. HASYLAB at DESY, Hamburg, is acknowledged for the provision of synchrotron radiation for the EXAFS spectroscopic measurements.

REFERENCES

1. Ullrich B, Sakai H, Segawa Y. *Thin Solid Films* 2001; **385**: 220.
2. Henglein A. *Chem. Rev.* 1989; **89**: 1861.
3. Ristova M, Ristov M. *Appl. Surf. Sci.* 2001; **181**: 68.
4. Tsuji M, Aramoto T, Ohyama H, Hibino T, Omura K. *Jpn. J. Appl. Phys.* 2000; **39**: 3902.
5. Kumazawa S, Shibutani S, Nishio T, Aramoto T, Higuchi H, Arita T, Hanafusa A, Omura K, Murozono M, Takakura H. *Sol. Energy Mater. Sol. Cells* 1997; **49**: 205.
6. Shanthi S, Subramanaian C, Ramasamy P. *Mater. Chem. Phys.* 1999; **58**: 44.
7. O'Brien P, Haggata S. *Adv. Mater. Opt. Electron.* 1995; **5**: 117.
8. Senthil K, Mangalaraj D, Narayandass SK. *Appl. Surf. Sci.* 2000; **169/170**: 476.
9. Laukaitis G, Lindroos S, Tamulevicius S, Leskela M. *Appl. Surf. Sci.* 2001; **185**: 134.
10. Maury F. *Chem. Vap. Depos.* 1996; **2**: 113.
11. Gleizes AN. *Chem. Vap. Depos.* 2000; **6**: 155.
12. Bochmann M, Webb K, Harman M, Hursthouse MB. *Angew. Chem. Int. Ed. Engl.* 1990; **29**: 638.
13. Fainer NI, Kosinova ML, Rumyantsev YM, Salman EG, Kuznetsov FA. *Thin Solid Films* 1996; **280**: 16.
14. O'Brien P, Walsh JR, Watson IM, Motevalli M, Henriksen L. *J. Chem. Soc., Dalton Trans.* 1996; **12**: 2491.
15. Cheon J, Kang H, Zink J. *Coord. Chem. Rev.* 2000; **200/202**: 1009.
16. Barreca D, Tondello E, Lydon D, Spalding TR, Fabrizio M. *Chem. Vap. Depos.* 2003; **9**: 93.
17. Armelao L, Barreca D, Bottaro G, Gasparotto A, Maragno C, Sada C, Spalding TR, Tondello E. *Electrochem. Soc. Proc.* 2003; **8**: 1104.
18. Barreca D, Gasparotto A, Maragno C, Tondello E, Sada C. *Chem Vap. Depos.* 2004; **10**: 229.
19. Cox MJ, Tiekink ERT. *Rev. Inorg. Chem.* 1997; **17**: 1.
20. Palaty S, Joseph R. *J. Appl. Polym. Sci.* 2000; **78**: 1769.
21. Iimura Y, Ito T, Hagihara H. *Acta Crystallogr. Sect. B* 1972; **28**: 2271.
22. Tomlin DW, Cooper TM, Zelmon DE, Gebeyehu Z, Hughes JM. *Acta Crystallogr. Sect. C* 1999; **55**: 717.
23. Tiekink ERT. *Acta Crystallogr. Sect. C* 2000; **56**: 1176.
24. Fenn JB, Mann M, Meng CK, Wong SF, Whitehouse CM. *Science* 1989; **246**: 64.
25. Cooks RG, Beynon JH, Caprioli RM, Lester GR. *Metastable Ions*. Elsevier: Amsterdam, 1973.
26. Rao SR. *Xanthate and Related Compounds*. Dekker: New York, 1971.
27. Valli M, Persson P, Persson I. *Acta Chem. Scand.* 1994; **48**: 810.
28. Pattrick RAD, England KER, Charnock JM, Mosselmans JFW. *Int. J. Min. Process.* 1999; **55**: 247.
29. Rodic D, Spasojevic V, Bajorek A, Oennerud P. *J. Magnet. Magnet. Mater.* 1996; **152**: 159.
30. Colthup NB, Powell LP. *Spectrochim. Acta* 1987; **43**: 317.
31. Weidlein J, Mueller U, Dehnicke K. *Schwingungsspektroskopie* (2nd edn). Georg Thieme, Verlag: Stuttgart, 1988.
32. Siiman O, Titus DD, Cowman CD, Fresco J, Gray HB. *J. Am. Chem. Soc.* 1974; **96**: 2353.
33. Little LH, Poling GW, Leja J. *Can. J. Chem.* 1961; **39**: 745.
34. Mattes R, Pauleickhoff G. *Spectrochim. Acta* 1974; **30**: 379.
35. Hunt MR, Kruger GA, Smith L, Winter G. *Aust. J. Chem.* 1971; **24**: 53.
36. Göpel W, Wiemhöfer HD. *Statistische Thermodynamik*. Spektrum Akadamische, Verlag: Berlin, 2000.
37. Yamasaki T, Nanjo M. *Sci. Rep. Rev. Inst.* 1969; **21**: 45.
38. Raston CL, White AH, Winter G. *Aust. J. Chem.* 1976; **29**: 731.
39. Ertel TS, Bertagnolli H, Hückmann S, Kolb U, Peter D. *Appl. Spectrosc.* 1992; **46**: 690.
40. Newville M, Livins P, Yakoby Y, Rehr JJ, Stern EA. *Phys. Rev. B* 1993; **47**: 14 126.
41. Gurman SJ, Binsted N, Ross I. *J. Phys. C* 1986; **19**: 1845.

Copyright © 2004 John Wiley & Sons, Ltd.